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### INFRA-RED TRANSPARENT MATERIALS.

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## Description

This invention relates to infra red and visible wavelengths transparent materials. Such materials are useful as windows and lenses for thermal imaging systems, either as a coating or as a self supporting layer.

Materials commonly used are germanium, zinc sulphide, and zinc selenide. All are relatively soft and therefore easily damaged. One method of protecting these soft materials is to coat them with a hard material. The coating most successful to date is a hard carbon that is diamond like in its hardness. This is described in GB-B-2,082,562. Disadvantages of this material are the interstitial graphitic inclusions which limit the optical transmission and the internal strain which prevents layers thicker than about 1  $\mu\text{m}$  being grown. An alternative coating of hard carbon includes a small amount of germanium to relieve stress and allow thicker coatings to be made; this is described in GB-A-2,129,833 and GB-A-2,165,266. Another coating having infra red transparency is described in Solar Energy, vol 19, pages 429-432, Blickensderfer et al, Spectral reflectance of  $\text{TiN}_x$  and  $\text{ZrN}_x$  films. Such nitride coatings are described for use as films in selective solar absorbers.

Ideally a hard coating should be transparent in the 3-5 and 8-14  $\mu\text{m}$  infra red wavebands, and also in the visible band i.e. about 0.4 to 0.7  $\mu\text{m}$ . It is further desirable that the coating is stable and transparent at high temperatures so that it may be used as a window for high temperature processes. A disadvantage of the hard carbon, and hard germanium carbon coatings is their high temperature performance. On heating to say 600 °C the carbon changes to a graphitic form which is absorbing to infra red radiation. These materials are also absorbing to visible light in useful thicknesses.

It is an object of this invention to provide a material that is infra red transparent over a wide band of wavelengths and elevated temperatures.

According to this invention an infra red and visible transparent material is formed of Zirconium nitride or Yttrium nitride also Cerium or Thorium or Europium nitride.

The material may be used as a coating on infra red transparent substrate material such as Ge, ZnS, ZnSe,  $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{Se}_3$ ; optically transparent material such as sodium, silica or lead glass; any suitable metal such as Cu, Al, alloys of Al, alloys of Fe or silvered surfaces; or as a self supporting layer in which case the supporting substrate is removed e.g. by etching. These infra red transparent materials Ge, etc., are transparent in the 1.9-2.7, 3-5 and 8-14  $\mu\text{m}$  wavebands. ZnS, ZnSe,  $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{Se}_3$  are also partly transmissive in the visible waveband. Glass is transparent up to about

2.5  $\mu\text{m}$  i.e. the visible and near infra red waveband. The coating is hard and may therefore be used for its abrasion resistant properties for example on infra red windows and lenses. Alternatively it may be used on metal to maintain a highly polished surface on components such as turbine blades and ductings. A further use on metals is to provide a hard wear resistant coating on cutting tools used on lathes etc.

The material may be formed by reactive sputtering using a target of Zr, Y, Ce, Eu or Th in a DC or RF glow discharge of the gases Ar and N.

According to this invention an optical component comprises a transparent substrate coated with a transparent thin layer of ZrN, YN, CeN, EuN or ThN, the component being transparent in the infra red (1.9-2.7, 3-5 and 8-14  $\mu\text{m}$ ) and in the visible band (0.4 to 0.7  $\mu\text{m}$ ) of wavelengths.

According to an aspect of this invention the reflecting surfaces of a direct view thermal imager are coated with a thin layer of ZrN, YN, CeN, ThN or EuN, transparent in both infra red (3 - 5, and 8 - 14  $\mu\text{m}$ ) and visible (0.4 - 0.7  $\mu\text{m}$ ) wavebands.

According to this invention a method of producing Zirconium, Yttrium, Cerium, Thorium or Europium nitride comprises the steps:- providing an anode and a cathode inside a vacuum chamber, arranging a target of Zr, Y, Ce, Th or Eu on the cathode, mounting a substrate to be coated opposite and spaced from the cathode, maintaining the substrate at a desired temperature of between 500 and 600 °C, flowing gases of argon and nitrogen through the chamber whilst maintaining a reduced pressure inside the chamber, providing a glow discharge plasma inside the chamber between the anode and cathode, whereby argon ions sputter off material from the target to combine with nitrogen on the substrate and form the desired coating transparent to visible and infra red wavelengths of 0.4 to 0.7  $\mu\text{m}$ , 3-5  $\mu\text{m}$  and 8-14  $\mu\text{m}$ .

The glow discharge may be provided by an R.F. or a D.C. electric field. Enhanced deposition rate may be provided by magnetron sputtering. The substrate to be coated may be mounted directly on the anode or spaced therefrom.

Alternatively the coatings may be grown by molecular beam epitaxy (MBE) growth apparatus, vapour phase epitaxial growth apparatus, or by a ceramic process. In this latter case a powder of Zr, Ce, Th, or Eu nitride is formed and milled to the required particle size, then pressed into a blank of the required shape and fired at an elevated temperature until a ceramic blank is formed.

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The invention will now be described, by way of example only, with reference to the accompanying drawings of which:-

Figure 1 is a cross sectional view of glow discharge apparatus,

Figure 2 is a sectional view of a component coated in the apparatus of figure 1,

Figures 3(a), (b), 4(a), (b) are graphs of transmission against wavelength for the component of figure 2.

Figure 5 is a diagrammatic view of a pyro-electric vidicon camera.

As shown in Figure 1 glow discharge apparatus comprises a vacuum tight chamber 1 containing an anode plate 2 and a cathode plate 3. The anode 2 is heated by a heater 4 and carries a substrate 5 to be coated. Examples of substrate materials are Ge, ZnS, ZnSe, and metals such as Cu, Al, silvered surfaces, and various alloys and steels. Both the chamber 1 and anode 2 are connected to earth. The cathode 3 carries a plate of target material 6, e.g. Zirconium (Zr) or Yttrium (Y), and is connected to an RF source 7 via a capacitor 8. Negative voltage developed at the cathode is measured by a D.C. voltmeter 9. Gas bottles 10, 11 supply nitrogen and argon through valves 12, 13, 14 into the chamber 1. A vacuum pump 15 removes gases from inside the chamber 1 via a restrictor valve 16.

Operation to grow a Zr, or Y nitride layer 17 transparent to a wide band of wavelengths, including the infra red and visible, is as follows: The target 6 and substrate 5 are mounted as shown on the cathode 3 and anode 2 respectively. The anode 2 and substrate 5 temperatures are raised to about 500 to 550 °C. Other temperatures may be used. However, below about 500 °C the grown layer becomes increasingly absorbing. Above about 600 °C there are practical difficulties in providing an anode/substrate holder and reliable resistance heaters. The pump 15 is operated to drop the pressure to about 40 Pa (30 millitorr) whilst nitrogen and argon gasses are admitted from the bottles 10, 11 and an RF D.C. bias of about -1 kV is applied to the cathode. This produces a plasma discharge between the anode 2 and cathode 3. Argon ions strike the target and remove atoms of the target material which combine with nitrogen in the plasma to deposit as a layer 17 of zirconium nitride or yttrium nitride on the substrate 5. For correct deposition parameters the layer is transparent to a wide band of wavelengths e.g. 0.4-16µm.

Ce, Th or Eu nitride coating layers are grown in a similar manner.

When growing Zr nitride the percentage of N to Ar is about 50%. For Y nitride the percentage of N to Ar is about 1%. Deposition rates are typically 0.2µm/hour for ZrN and 0.4µm/hour for YN. These rates may be increased by magnetron sputtering

techniques.

Prior to coating the substrates may be cleaned for example by Ar ion bombardment. This may be achieved by mounting the substrate on the cathode 3, admitting Ar into the chamber whilst reducing the pressure to about 26.7 Pa (20 millitorr). A glow discharge is initiated and maintained for about 5 minutes. A similar cleaning process may be made to the target 6.

Coatings of ZrN and YN have excellent adhesion to most metals, e.g. Al, Duraluminium, Cu, stainless steel and Ag. The adhesion on Ge, ZnSe, and ZnS is good but less than for the metals. To improve adhesion on Ge, ZnSe, and ZnS, a very thin bonding layer (less than 0.5µm) of  $\text{Ge}_x\text{C}_{1-x}$  ( $0 < x < 1$ ) may be deposited from a vapour of Ge and C. Typically only a few nanometres (Angstroms) thick layer is needed. For example the bonding layer may be 1 to 100 typically 10 nm (10 to 1,000 typically 100 Angstroms) thick. Being so thin the bonding layer has negligible effect on transmission at any wavelength. The Ge and C vapour may be produced in the apparatus of Figure 1 using a glow discharge to dissociate germane and hydrocarbon gases, without sputtering from a Zr or Y target. Other bonding materials are Ge, Si, and  $\text{Si}_x\text{C}_{1-x}$  produced as for GeC. Silicon alone, with carbon, or as an oxide may be used. This can be deposited using a silane feedstock.

Figures 3(a), (b) show the transmittance values for a Ge substrate and for a Ge substrate coated with 0.5µ of ZrN, the coated substrate being the upper trace. Figures 4(a), (b) show transmittance values for Ge and Ge coated with a 1µm thick layer of YN. Both Figures 3 and 4 show excellent transmittance from 2.5µm out to 12µm and 14µm for ZrN and YN respectively.

Coating thickness for anti-reflection properties can be calculated as follows:

$$2n:d = \lambda/2$$

where

$n$  is refractive index of coating

$d$  is coating thickness

$\lambda$  is wavelength of radiation concerned.

For good matching  $n_1 = \sqrt{n_0 \times n_2}$

where  $n_0$  and  $n_2$  are the refractive indexes of the material either side of the coatings. For air  $n_0 = 1$ , for bulk Ge  $n_2 = 4$ .

The refractive index was found to be 2.1 for both ZrN and YN which is ideal for use as an antireflection coating on Ge lenses. For use in 8 - 14 µm thermal imagers the antireflection coating would be 1.2 µm thick for a  $\lambda/4$  thickness at 10 µm wavelength.

The coatings were found to be chemically inert and very hard, having a hardness value >2000

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Knoop. This approaches that of diamond-like carbon coatings of the prior art. Unlike these diamond-like coating the ZnN and YN coatings are stable at temperatures in excess of 500 °C for long periods.

These properties make the coating useful as windows on tanks and other vehicles where the combination of windscreen wipers and sand make it essential that very hard coatings are used. Behind these windows thermal imagers are arranged to view the thermal scene. Prior to the introduction of hard carbon coatings the lifetime of such windows was very short. An advantage of coatings of the present invention over hard carbon coatings is their optical transparency. This allows both thermal and optical imaging systems to be arranged behind the windows of optically and infra-red transmitting material, e.g. ZnS, ZnSe, As<sub>2</sub>S<sub>3</sub>, As<sub>2</sub>Se<sub>3</sub> window.

The refractive index of ZnN, YN at about 2.1 is similar to that of ZnS, ZnSe, and sodium glasses. Thus coatings directly on such substrates are protective without being anti-reflective. To provide anti-reflective properties a multi coated layer must be used. For example on ZnS or ZnSe substrates a GeC  $\lambda/4$  layer with an  $n = 3$  may be used directly on the substrate. As taught in GB-A-2,129,833 the value of  $n$  is variable with the ratio of Ge to C. Next a layer of GeC with a graded refractive index (effective  $n = 4$ ) is used by varying the Ge:C ratio. The final layer is of a  $\lambda/4$  thickness (e.g. 1.2  $\mu\text{m}$  at 10  $\mu\text{m}$  wavelength) of ZnN, or YN.

Alternatively on ZnS, ZnSe substrates a thick coating, e.g. up to 20  $\mu\text{m}$  or more, may be used. This thick coating gives added mechanical protection. A final anti-reflection coating of ThF may be deposited. This is not very hard but for some applications gives an adequate protection.

Another use of the coatings of the present invention is as a front coating on Ge lenses. Figure 5 shows a pyroelectric vidicon camera used by fire fighting services to see through smoke inside burning buildings. These known cameras 20 have a front Ge lens 21 plus other smaller lenses 22 focussing the thermal scene onto a pyroelectric detector tube 23. Output from the tube 23 is used by control circuits 24 to modulate a cathode ray tube (CRT) 25 and form a visible display 26 of the thermal scene. The front lens 21 is coated with ZnN or YN so that dirt is easily removed without damaging the soft Ge material.

Similarly the front lens of optical cameras used in surveying sewers etc may be coated with ZnN or YN to prevent damage.

The high temperature stability enables the material to be used on windows subject to adverse conditions such as in furnaces etc.

Another use of the invention is in direct view thermal imagers. These are known imagers, e.g. GB-A 2,291,196, having rotating polygons and/or

flapping mirrors to sweep scan the image of a thermal scene onto an infra red detector. Output from the detector modulates the light output from a lamp such as a light emitting diode (LED). The rotating polygons and/or flapping mirror also scans the LED into an eye piece for observation by an operator. The scanning mechanism is thus used to scan infra red and visible light.

A problem with rotating polygons is tarnishing of the highly polished reflecting surfaces. One solution to this problem is disclosed in GB-A-2,067,304. A thin layer of infra red transparent amorphous carbon is deposited on the reflecting surfaces. Such a solution is only useful in standard imagers where the detector output modulates a CRT display. The hard carbon is opaque to visible light. Therefore it cannot be used in direct view thermal imagers.

However this problem can be overcome by use of the present invention. Reflecting surfaces are protected by a thin coating of ZnN, YN, CeN, ThN or EuN, transparent at infra red and optical wavelengths. The coating may be less than 1  $\mu\text{m}$  - typically about 0.1 to 0.2  $\mu\text{m}$  thick.

Self supporting thick, e.g. 10 to 1000  $\mu\text{m}$  or more, layers may be grown e.g. on Al substrates, and the substrate subsequently removed by an etchant such as nitric acid, or hydrochloric acid.

### Claims

1. A material transparent at 3-5 and 8-14  $\mu\text{m}$  infra red wavebands and 0.4 to 0.7  $\mu\text{m}$  visible wavelengths in layer on a substrate, sheet or bulk form of Zirconium nitride, Yttrium nitride, Cerium nitride, Thorium nitride, or Europium nitride.
2. An optical component formed of an infra red transparent substrate coated on at least one surface with the material of claim 1.
3. The component of claim 2 wherein the substrate is Ge, ZnS, ZnSe, As<sub>2</sub>S<sub>3</sub>, As<sub>2</sub>Se<sub>3</sub>.
4. The component of claim 2 wherein a bonding layer less than 0.5  $\mu\text{m}$  thick is formed on the substrate, with the coating on top of the bonding layer.
5. The component of claim 4 wherein the bonding layer is of Ge, Si, Ge<sub>x</sub>C<sub>1-x</sub> or Si<sub>x</sub>C<sub>1-x</sub>, 0 < x < 1.
6. An optical component formed of an optically transparent substrate coated on at least one surface with the material of claim 1.

7. The component of claim 6 wherein the substrate is sodium glass.
8. The component of claims 2 wherein the coating has a thickness giving an anti-reflective coating at a specified wavelength.
9. An infrared and optically reflecting element comprising a highly reflecting surface coated with the material of claim 1.
10. The element of claim 9 wherein the highly reflecting surface is a metallic surface and the coating is a layer less than  $1\mu\text{m}$  thick.
11. A method of producing the material of claim 1 comprising the steps:-  
providing an anode and a cathode inside a vacuum chamber,  
arranging a target of Zr, Y, Ce, Th or Eu on the cathode,  
mounting a substrate to be coated opposite and spaced from the cathode, maintaining the substrate at a desired temperature of between  $500$  and  $600^\circ\text{C}$ ,  
flowing gases of argon and nitrogen through the chamber whilst maintaining a reduced pressure inside the chamber,  
providing a glow discharge plasma inside the chamber between the anode and cathode, whereby argon ions sputter off material from the target to combine with nitrogen on the substrate and form the desired coating transparent to visible and infra red wavelengths of  $0.4$  to  $0.7\mu\text{m}$ ,  $3-5\mu\text{m}$  and  $8-14\mu\text{m}$ .
12. The method of claim 11 wherein, prior to growing the coating, a bonding layer of Ge, Si  $\text{Ge}_x\text{C}_{1-x}$ , or  $\text{Si}_x\text{C}_{1-x}$  of thickness less than  $0.5\mu\text{m}$  is grown,  $0 < x < 1$ .

#### Patentansprüche

1. Material, das in den Infrarotwellenlängenbereichen von  $3$  bis  $5\mu\text{m}$  und von  $8$  bis  $14\mu\text{m}$  sowie im sichtbaren Wellenlängenbereich von  $0,4$  bis  $0,7\mu\text{m}$  durchlässig ist, das in Form einer Schicht auf einem Träger oder einer selbsttragenden Folie oder in massiver Form vorliegt und aus Zirkoniumnitrid, Yttriumnitrid, Cernitrid, Thoriumnitrid oder Europiumnitrid besteht.
2. Optische Komponente, die aus einem infrarotlichtdurchlässigen Träger, der auf mindestens einer Oberfläche mit dem Material nach Anspruch 1 beschichtet ist, besteht.

3. Komponente nach Anspruch 2, wobei des Träger Ge, ZnS, ZnSe,  $\text{As}_2\text{S}_3$  oder  $\text{As}_2\text{Se}_3$  ist.
4. Komponente nach Anspruch 2, wobei eine verbindende Zwischenschicht, die weniger als  $0,5\mu\text{m}$  dick ist, auf dem Träger gebildet ist, auf der die Beschichtung vorgesehen ist.
5. Komponente nach Anspruch 4, dadurch gekennzeichnet, daß die verbindende Zwischenschicht aus Ge, Si,  $\text{Ge}_x\text{C}_{1-x}$  oder  $\text{Si}_x\text{C}_{1-x}$  besteht, wobei  $0 < x < 1$  ist.
6. Optische Komponente, die aus einem optisch durchlässigen Träger, der auf mindestens einer Oberfläche mit dem Material nach Anspruch 1 beschichtet ist, besteht.
7. Komponente nach Anspruch 6, wobei der Träger Natriumglas ist.
8. Komponente nach Anspruch 2, wobei die Beschichtung eine Dicke hat, die einen Antireflexbelag bei einer bestimmten Wellenlänge ergibt.
9. Infrarotlicht und sichtbares Licht reflektierendes Element, das eine hochreflektierende Oberfläche aufweist, die mit dem Material nach Anspruch 1 beschichtet ist.
10. Element nach Anspruch 9, wobei die hochreflektierende Oberfläche eine metallische Oberfläche ist und die Beschichtung eine Schichtdicke von weniger als  $1\mu\text{m}$  aufweist.
11. Verfahren zur Herstellung des Materials nach Anspruch 1, das folgende Schritte umfaßt:
- Anordnen einer Anode und einer Kathode in einer Vakuumkammer,
  - Anbringen eines Targetmaterials aus Zr, Y, Ce, Th oder Eu auf der Kathode,
  - Anbringen eines zu beschichtenden Trägers gegenüber und beabstandet von der Kathode,
  - Aufrechterhaltung einer gewünschten Temperatur des Trägers zwischen  $500$  und  $600^\circ\text{C}$ ,
  - Durchleiten von gasförmigem Argon und Stickstoff durch die Vakuumkammer unter Aufrechterhaltung eines verminderten Drucks in der Vakuumkammer, und
  - Erzeugung eines Glimmentladungs-Plasmas in der Vakuumkammer zwischen der Anode und der Kathode, wobei die Argonionen Substanz vom Targetmaterial zerstäuben, die mit dem Stickstoff auf dem Träger abreagiert und

die gewünschte Beschichtung bildet, die für sichtbares Licht im Wellenlängenbereich von 0,4 bis 0,7  $\mu\text{m}$  und für Infrarotlicht in den Wellenlängenbereichen von 3 bis 5  $\mu\text{m}$  und von 8 bis 14  $\mu\text{m}$  durchlässig ist.

12. Verfahren nach Anspruch 11, wobei vor dem Abscheiden der Beschichtung eine verbindende Zwischenschicht aus Ge, Si,  $\text{Ge}_x\text{C}_{1-x}$  oder  $\text{Si}_x\text{C}_{1-x}$  mit  $0 < x < 1$  aufwachsen gelassen wird, deren Dicke kleiner als 0,5  $\mu\text{m}$  ist.

#### Revendications

1. Matériau transparent dans les bandes de longueurs d'onde infrarouges de 3 à 5  $\mu\text{m}$  et de 8 à 14  $\mu\text{m}$  et dans les bandes de longueurs d'onde visibles de 0,4 à 0,7  $\mu\text{m}$ , sous forme d'une couche placée sur un substrat, sous forme d'une feuille ou sous une forme massive, constitué de nitrure de zirconium, de nitrure d'yttrium, de nitrure de cérium, de nitrure de thorium ou de nitrure d'euporium.
2. Élément optique formé d'un substrat transparent à la lumière infrarouge, revêtu, sur une face au moins, du matériau selon la revendication 1.
3. Élément selon la revendication 2, dans lequel le substrat est formé de Ge, ZnS, ZnSe,  $\text{As}_2\text{S}_3$  ou  $\text{As}_2\text{Se}_3$ .
4. Élément selon la revendication 2, dans lequel une couche de liaison d'épaisseur inférieure à 0,5  $\mu\text{m}$  est formée sur le substrat, le revêtement étant placé sur la couche de liaison.
5. Élément selon la revendication 4, dans lequel la couche de liaison est formée de Ge, Si  $\text{Ge}_x\text{C}_{1-x}$  ou  $\text{Si}_x\text{C}_{1-x}$  avec  $0 < x < 1$ .
6. Élément optique formé d'un substrat transparent optiquement revêtu sur une face au moins du matériau selon la revendication 1.
7. Élément selon la revendication 6, dans lequel le substrat est un verre sodique.
8. Élément selon la revendication 2, dans lequel le revêtement a une épaisseur telle qu'il forme un revêtement antiréfléchissant à une longueur d'onde spécifiée.
9. Élément infrarouge optiquement réfléchissant comprenant une surface très réfléchissante revêtue du matériau selon la revendication 1.

10. Élément selon la revendication 9, dans lequel la surface très réfléchissante est une surface métallique et le revêtement est une couche d'épaisseur inférieure à 1  $\mu\text{m}$ .

11. Procédé de fabrication du matériau selon la revendication 1, comprenant les étapes suivantes :

la disposition d'une anode et d'une cathode dans une chambre sous vide,

la disposition d'une cible de Zr, Y, Ce, Th ou Eu sur la cathode,

le montage d'un substrat qui doit être revêtu en face de la cathode et à distance de celle-ci, avec maintien du substrat à une température voulue comprise entre 500 et 600 °C,

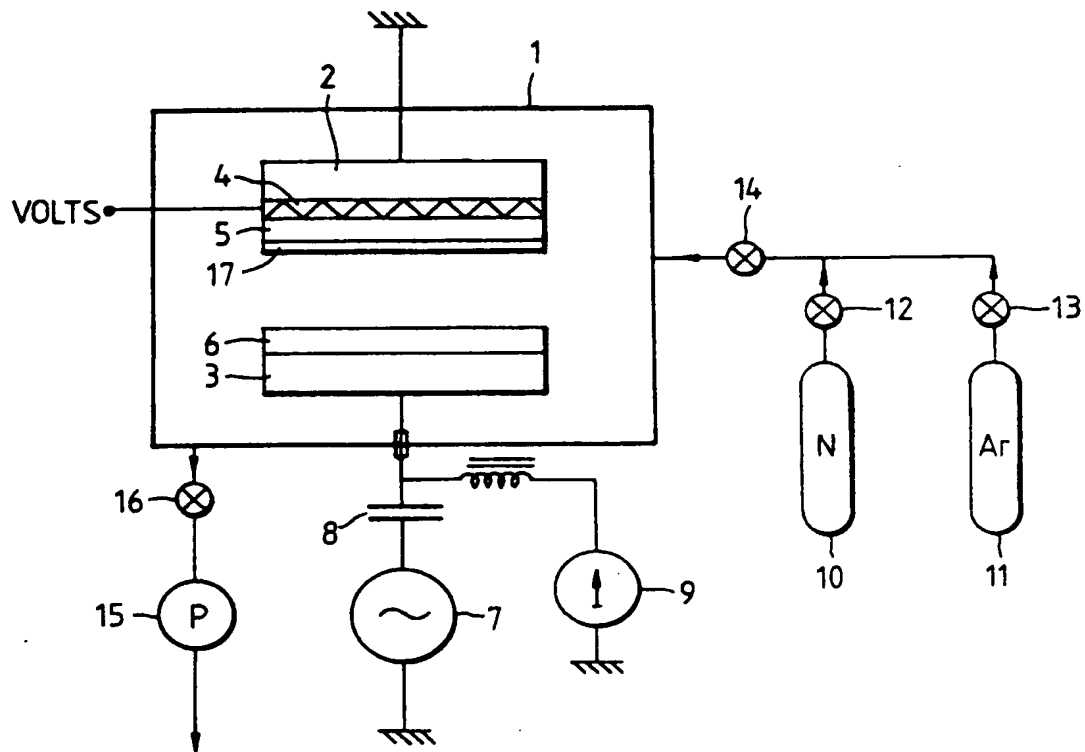
la circulation d'argon et d'azote gazeux dans la chambre avec maintien d'une pression réduite dans la chambre, et

la création d'un plasma par décharge lumineuse dans la chambre entre l'anode et la cathode,

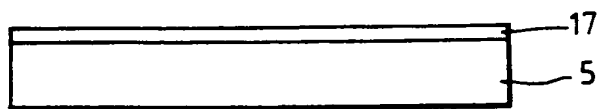
si bien que les ions argon pulvérisent la matière de la cible qui se combine avec l'azote sur le substrat et forme le revêtement voulu transparent aux longueurs d'onde visibles et infrarouges entre 0,4 et 0,7  $\mu\text{m}$ , 3 et 5  $\mu\text{m}$ , et 8 et 14  $\mu\text{m}$ .

12. Procédé selon la revendication 11, dans lequel, avant la croissance du revêtement, une couche de liaison formée de Ge, Si,  $\text{Ge}_x\text{C}_{1-x}$  ou  $\text{Si}_x\text{C}_{1-x}$ , avec  $0 < x < 1$ , est formée par croissance avec une épaisseur inférieure à 0,5  $\mu\text{m}$ .

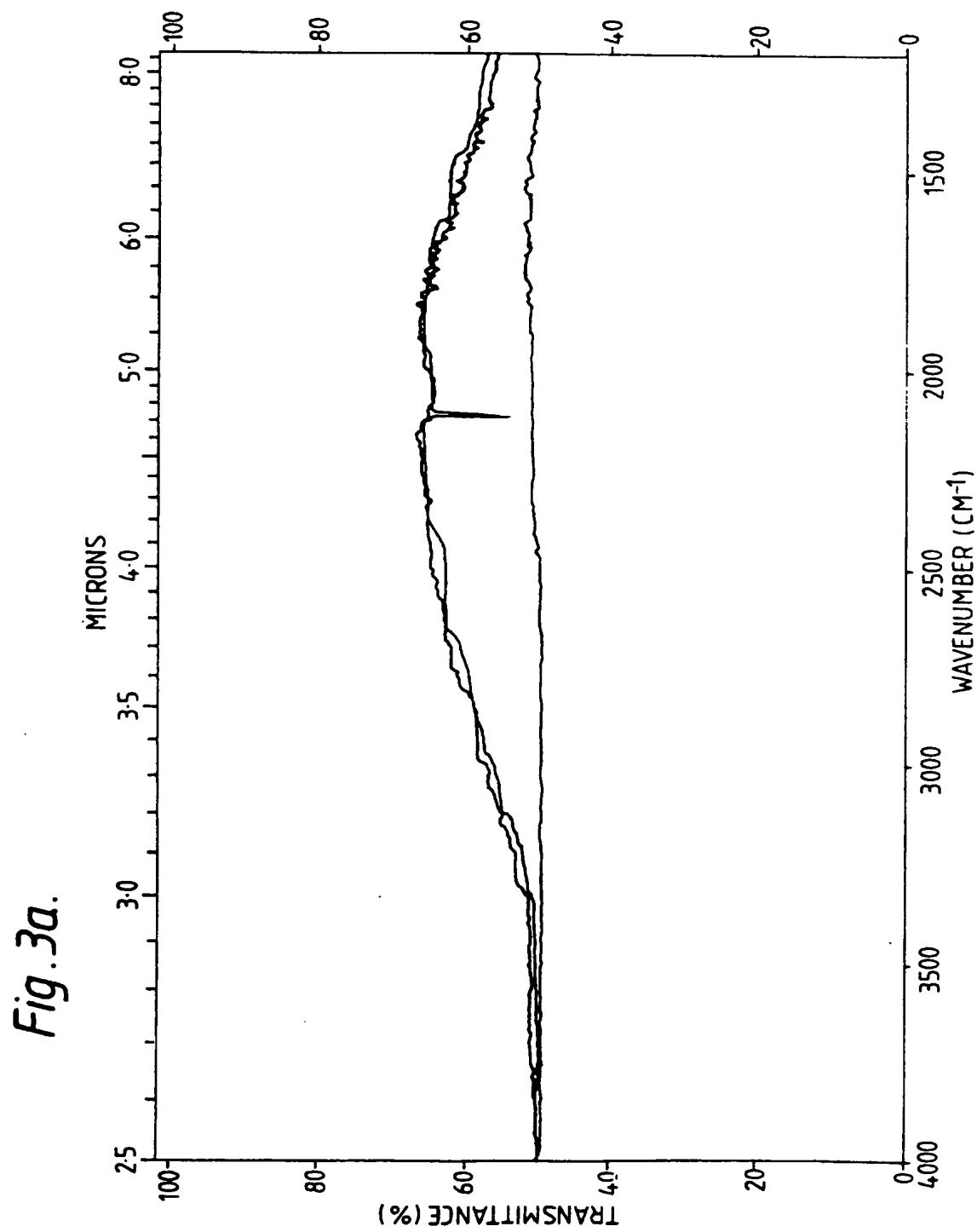
*Fig. 1.*



*Fig. 2.*

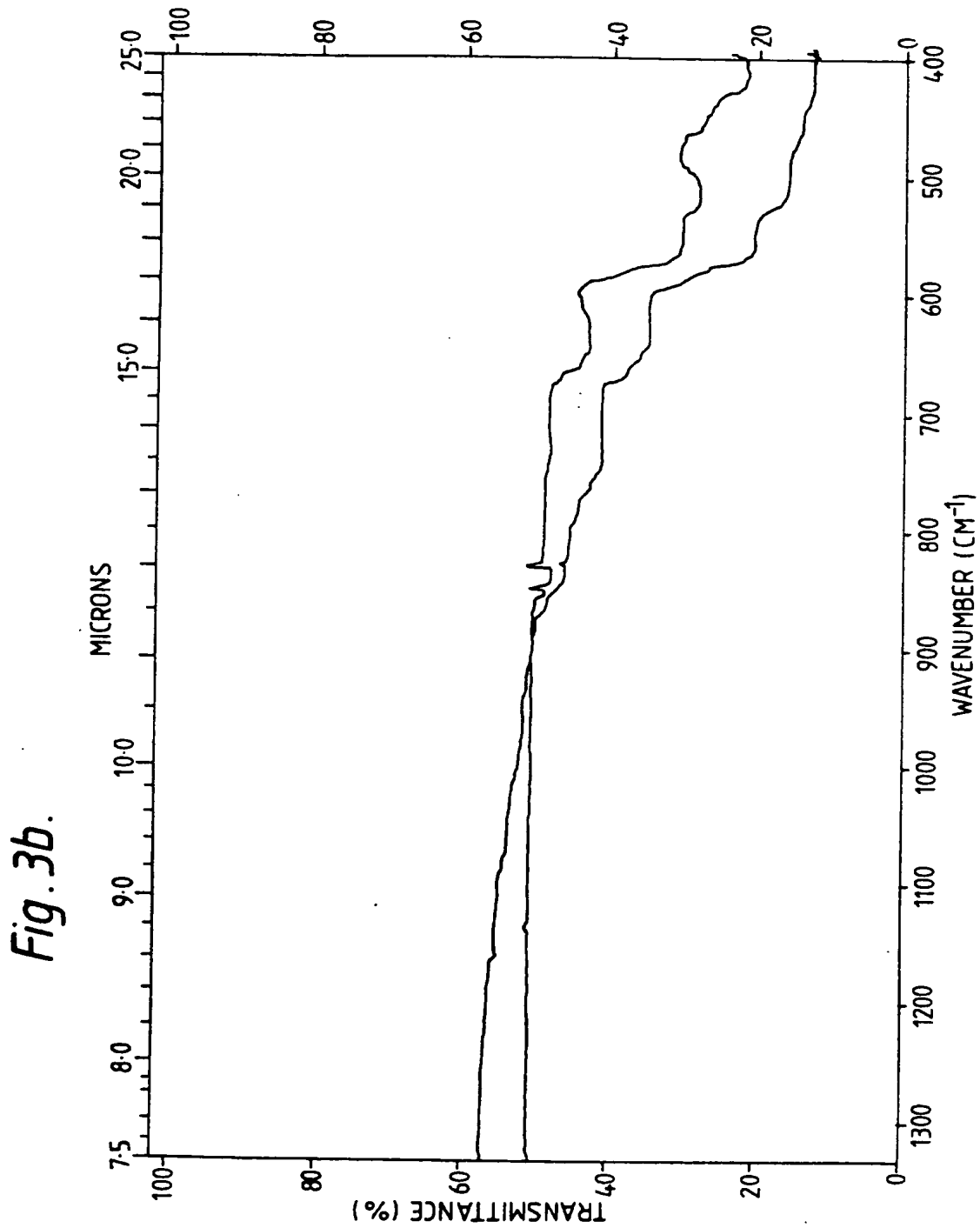


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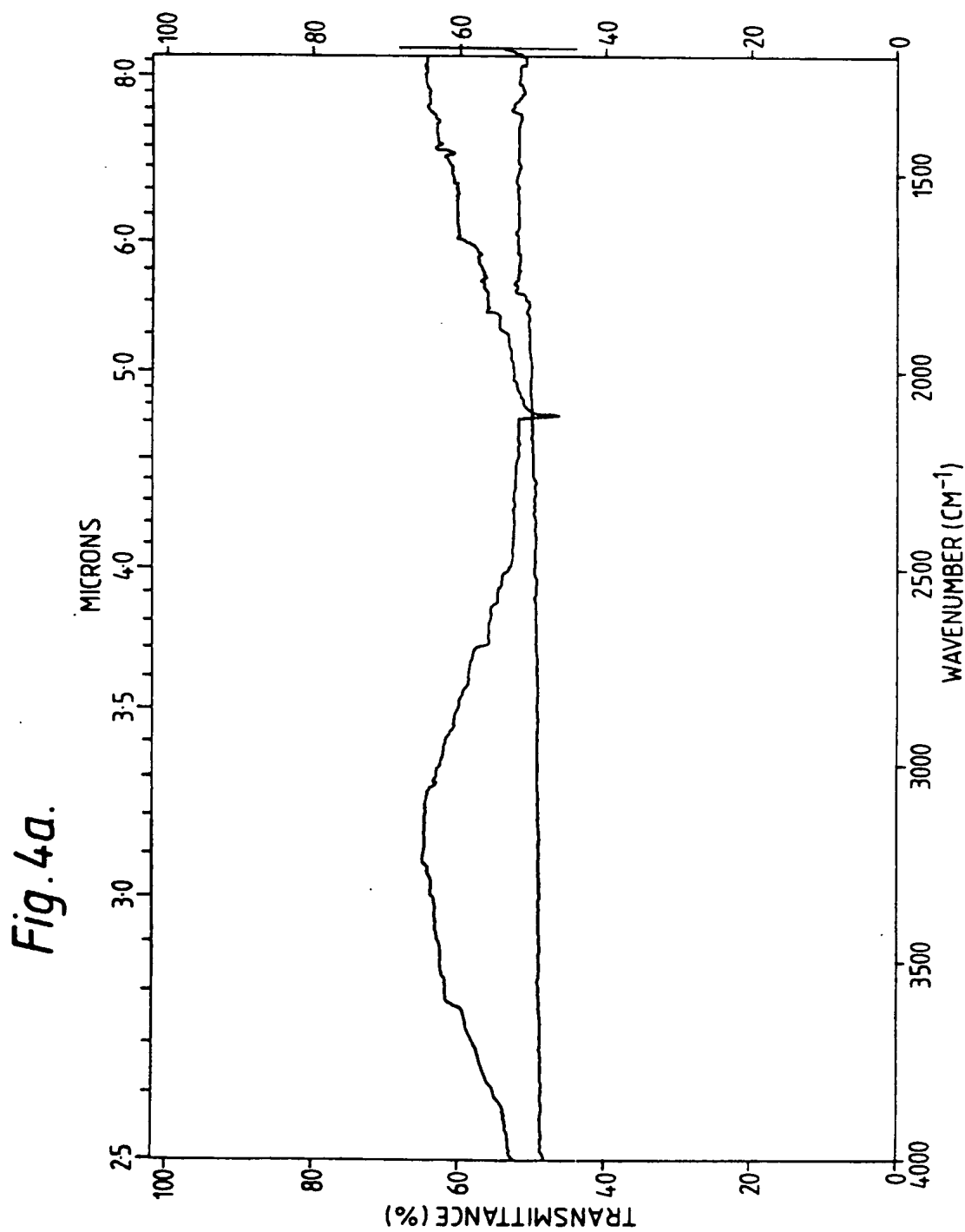




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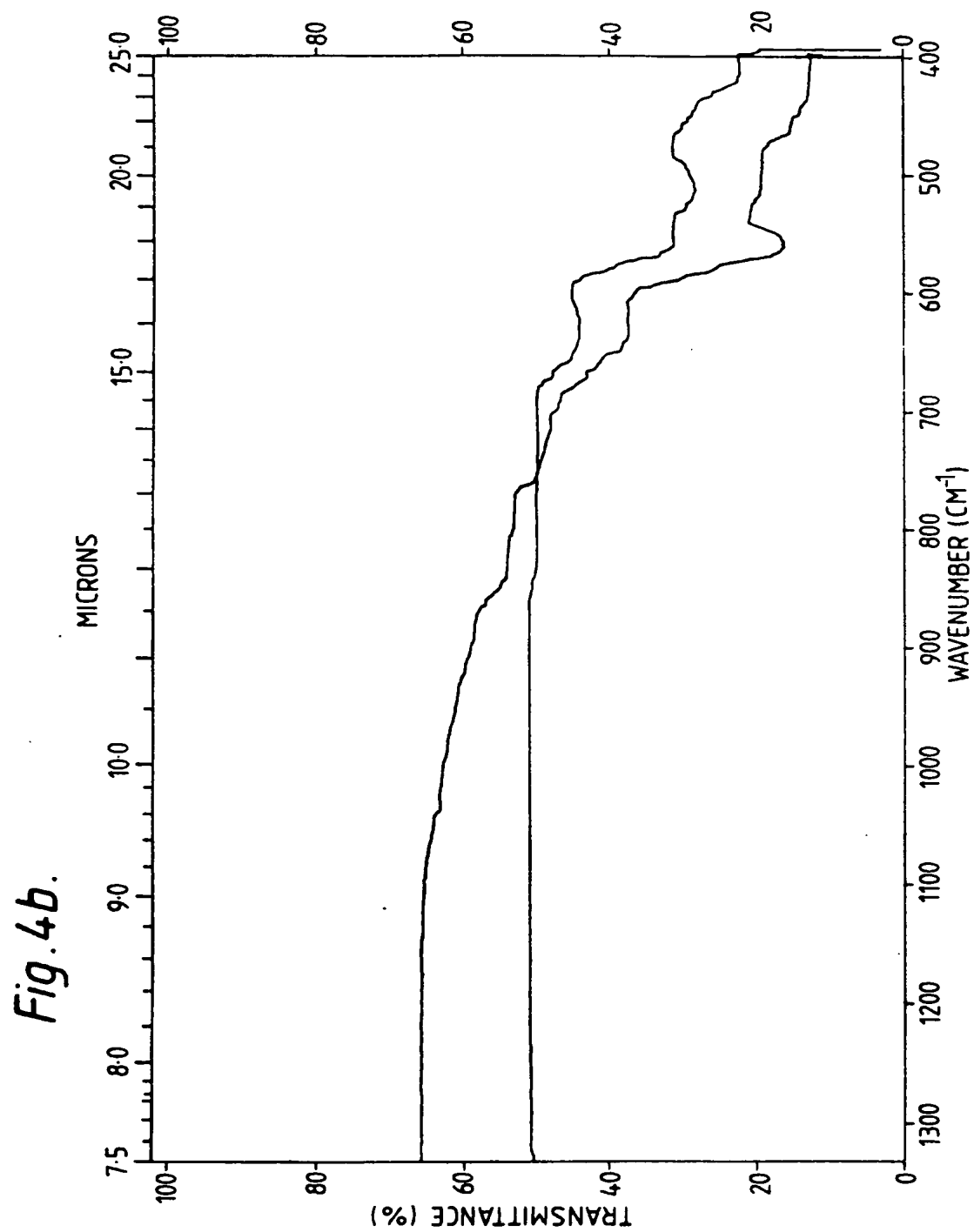


Fig. 5.

Fig. 5.